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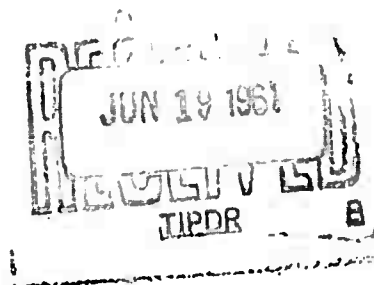
CHEMICAL KINETICS IN SHOCK-HEATED AIR

C. B. Ludwig  
K. G. P. Sulzmann

February 1, 1961

This research was supported by the  
Army Research Guided Missile Agency  
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## CHEMICAL KINETICS IN SHOCK HEATED AIR

C. B. Ludwig  
K. G. P. Sulzmann

### ABSTRACT

The concentration profile and the reaction rates of a postulated reaction scheme have been estimated. It is shown that the contributions of the rates of formation and decomposition of dominant species ( $N_2$ ,  $O_2$ , N, O, and NO) involving these species only are greater by orders of magnitude than the contributions involving the added minor constituents ( $N_2O$ ,  $NO_2$ ,  $NO_3$ , and  $O_3$ ).

### INTRODUCTION

In considering chemical kinetics in shock-heated air, one is confronted with a great number of reactions. Duff and Davidson<sup>1</sup> have selected a limited scheme of ten reactions in which the species  $N_2$ ,  $O_2$ , N, O, and NO are involved. The purpose of this report is to estimate the concentration profile of a number of additional species such as  $O_3$ ,  $N_2O$ ,  $NO_2$  and  $NO_3$ . This estimate is based on the assumptions that the solution of the limited scheme remains unperturbed and that the concentrations of the additional species are in a steady-state. The mathematical verification of these assumptions would require the simultaneous solution of the expanded scheme. However, it can be shown for the three shock conditions considered that the concentrations of the additional species are smaller by orders of magnitude than most of the major constituents. Also, the contributions of the additional species to the rates of formation and decomposition of the major constituents are insignificantly small. Therefore, it might be expected that the result of the "zero-order perturbation"

does not lead to contradictions. The reaction rate coefficients have been taken from the literature where available or else have been calculated by using simple collision theory to estimate the frequency factors. No attempt has been made to determine activation energies.

This report supercedes "Chemical Kinetics Behind Strong Shock Waves II. Review of chemical reactions occurring in a  $N_2 - O_2$  mixture at 6000° to 10,000°K."<sup>6</sup>

### ASSUMPTIONS

It is assumed that a mixture of 78% nitrogen and 22% oxygen exists in equilibrium at 300°K and 1-mm Hg pressure. After a normal shock wave has passed, the temperature is raised to value  $T_s$ , at which the translational, rotational, and vibrational degrees of freedom of the molecules are assumed to be equilibrated. Furthermore, it is assumed that no chemical reactions occur during the process of establishing the temperature  $T_s$ , i.e., the reactions are considered to be frozen throughout the translational and rotational relaxation zone. Then the chemical reactions will start at a surface behind the shock front at which the temperature  $T_s$  is established; this surface is taken as the origin of a coordinate system in which the reaction history is measured. Change of electronic states (in particular, ionization) are not included here. An estimate of the actual temperature  $T_s$  and the relaxed density at the origin of the reaction history are obtained by taking the data calculated by Duff and Davidson.<sup>1</sup> These data are presented in the tabulation for the three shock conditions treated here.

$\underline{M_s}$	$\underline{T_s}$	$\underline{T_t}$	$\underline{T_e}$	$\underline{\theta_t^I}$	$\underline{\theta_t^{II}}$
9.96	5,000	4,000	3,400	30	800
12.06	7,000	5,000	4,600	8	50
14.71	10,000	6,000	5,500	100	3.3



where

- $T_s$  = Temperature ( $^{\circ}\text{K}$ ) at points (origin of reaction history taken from Duff),
- $T_t$  = Assumed temperature value in the transition zone at which the calculations have been performed,
- $\theta_t^{\text{I}}$  = Travelling time ( $\mu\text{sec}$ ) for a typical mass element behind the shock front until N reaches a maximum
- $\theta_t^{\text{II}}$  = Travelling time ( $\mu\text{sec}$ ) for a typical mass element behind the shock front until NO reaches a maximum, and
- $T_e$  = Equilibrium temperature taken from equilibrium calculations made by Hochstim.<sup>3</sup>

The extent of the reaction scheme can further be limited by conditions which are specified in the next section. In many of the reactions, a third body will participate which remains unchanged and is labeled (M). This symbol stands for any one of the species present in the mixture. Although the rate coefficients for a third-body reaction might be different for different kinds of third bodies (M), this effect has been neglected in this study.

#### NITROGEN-OXYGEN REACTIONS

The number of possible reactions which might be conceived a priori between  $\text{N}_2$  and  $\text{O}_2$  is very large, even when reactions involving radiation and ionization processes are excluded. However, with the following obvious restrictions which are valid under the experimental conditions encountered, the reaction scheme can already be reduced rationally:

1. Only collisions up to three bodies will be considered in which case, however, the third body must remain unchanged, i.e., the third body is supposed to be of the type (M).<sup>†</sup>

---

<sup>†</sup>With this condition, reactions of the kind  $\text{O}_3 + \text{NO} + \text{NO} = \text{NO}_2 + \text{NO}_3$ ,  $\text{O}_3 + \text{N} + \text{N} = \text{N}_2\text{O} + \text{O} + \text{O}$ ,  $3 \text{NO} = \text{N}_2\text{O} + \text{NO}_2$  etc., are excluded. This seems well founded since the probability of this kind of three-body collision is very small.

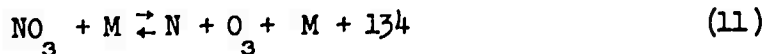
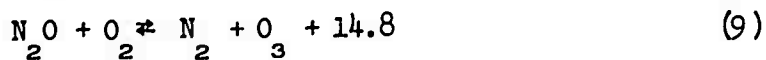
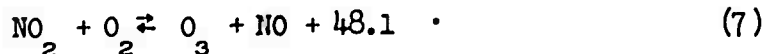
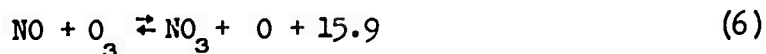
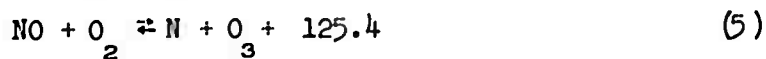
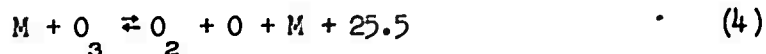
2. Higher nitrogen oxides such as  $N_2O_3$ ,  $N_2O_4$ , will be neglected because they are highly unstable under the conditions considered.
3. Reactions whose heat of formation exceeds 250 kcal/mole will not be considered because of their low efficiency under the conditions considered.

For each reaction listed in the following, the heat of formation in kilocalories is given. In the adopted notation, the endothermic processes are from left to right. The reaction scheme restricted by the above assumption is listed in six related groups. The reactions considered by Duff and Davidson<sup>1</sup> are indicated by an asterisk.

Group 1. Oxygen and Nitrogen Dissociation

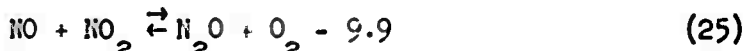
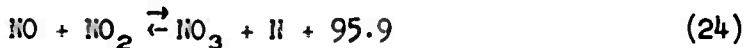
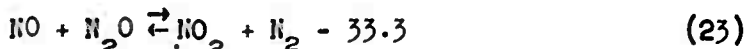
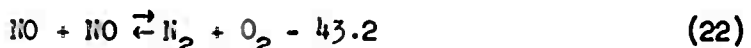
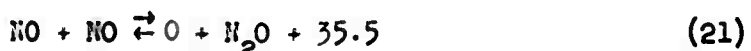
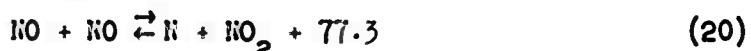
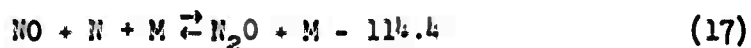
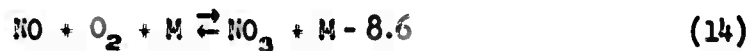
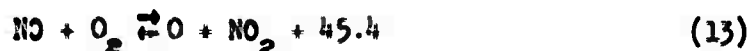


Group 2. Reaction Involving Ozone



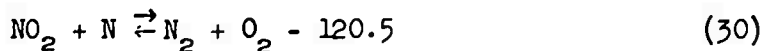
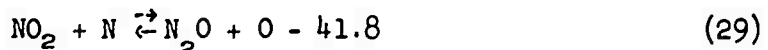
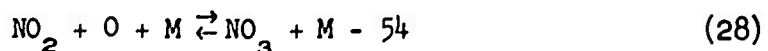
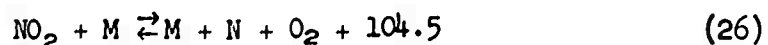
Group 3. Reactions involving NO

Besides the reactions (5), (6), and (7), there are:



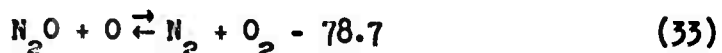
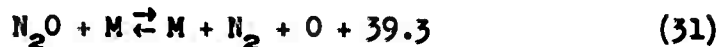
Group 4. Reactions involving NO<sub>2</sub>

Besides the reactions (7), (8), (16), (13), (20), (23), (24), (25), and (34), there are:



Group 5. Reactions involving  $N_2O$

Besides the reactions (25), (17), (9), (21), (29), (19), and (23), there are:



Group 6. Reactions involving  $NO_3$

These reactions have been given previously in (6), (10), (11), (14), (24), (27), (28), and (34).

In the following tables the heat of formation, the equilibrium constants of the 34 reactions, and the reaction rate constants are listed.

<u>Specie</u>	<u>Heat of Formation, kcal</u>	<u>Source</u>
$N_2$	0	Rossini, Bichowsky <sup>4</sup>
$O_2$	0	Rossini, Bichowsky <sup>4</sup>
N	+ 112.5	Gilmore <sup>5</sup>
O	+ 59.0	Gilmore <sup>5</sup>
NO	+ 21.6	Rossini, Bichowsky <sup>4</sup>
$O_3$	+ 34.5	Rossini, Bichowsky <sup>4</sup>
$NO_2$	+ 8.0	Rossini, Bichowsky <sup>4</sup>
$N_2O$	+ 19.7	Rossini, Bichowsky <sup>4</sup>
$NO_3$	+ 13.0	Rossini, Bichowsky <sup>4</sup>

Some of the equilibrium constants are taken from Davidson,<sup>2</sup> and the others are calculated by

$$K = \frac{\prod_1 n^{b_1} (B_1)}{\prod_1 n^{a_1} (A_1)} = A e^{-E/RT}$$

$$\ln A = \left( \sum_1 a_1 - \sum_1 b_1 \right) (\ln RT + \xi) + \sum_1 b_1 \ln Q_p(B_1) - \sum_1 a_1 \ln Q_p(A_1)$$

where  $\xi$  = unit conversion factor = + 3.722 and  $Q_p$  the partition function. The following values for  $Q_p$  have been selected (at 5,000°K)

Specie	$\ln Q_p$	Source
N <sub>2</sub>	30.141	Gilmore <sup>5</sup>
O <sub>2</sub>	32.187	Gilmore <sup>5</sup>
N	22.984	Gilmore <sup>5</sup>
O	23.968	Gilmore <sup>5</sup>
NO	32.647	Gilmore <sup>5</sup>
NO <sub>2</sub>	39.860	Gilmore <sup>5</sup>
N <sub>2</sub> O	37.971	Hochstim <sup>3</sup>
NO <sub>3</sub>	43.900	Davidson <sup>2</sup>
O <sub>3</sub>	40.120	Gilmore <sup>5</sup>

A list of the equilibrium constants follows:

# EQUILIBRIUM CONSTANTS

(Source •Davidson •Calculated)

Reaction No.	Pre-Exponential Factor	Activation Energy, cal	Dimensions	Reaction No.	Pre-Exponential Factor	Activation Energy, cal	Dimensions
1*	17.0	118,000	mole/cc	18*	0.26	- 75,100	-
2**	18.2	225,000	mole/cc	19**	0.16	110,600	-
3*	0.22	93,500	-	20**	0.037	77,300	-
4*	77.0	25,500	mole/cc	21**	0.035	35,500	-
5**	0.18	125,400	-	22*	0.048	- 43,200	-
6**	$7.55 \times 10^{-3}$	15,900	-	23**	0.54	- 33,300	-
7*	1.4	48,100	-	24**	$3.6 \times 10^{-3}$	95,900	cc/mole
8**	2.0	80,000	-	25**	0.073	- 9,900	-
9**	1.11	14,800	-	26**	0.073	104,500	mole/cc
10**	$3.44 \times 10^{-2}$	91,000	-	27**	131.0	64,000	-
11**	525.0	134,000	mole/cc	28*	$10^{-3}$	- 54,000	cc/mole
12**	4.02	149,000	mole/cc	29**	0.41	- 41,800	-
13**	0.37	45,400	-	30**	0.6	- 120,500	-
14**	$3.2 \times 10^{-4}$	- 8,600	cc/mole	31*	$1.3 \times 10^3 (300/7)$	39,300	mole/cc
15*	0.2	31,900	-	32**	140.0	105,800	-
16*	$9.4 \times 10^{-3}$	- 72,600	cc/mole	33*	7.3	- 78,700	-
17**	113.00	- 114,400	cc/mole	34**	23.8	- 18,600	-

REACTION NO.	REACTION RATE		TEMPERATURE, °K		SOURCE	
			5000	6000		
1	$3.1 \times 10^{13} \exp (-118,000/RT)$ $3 \times 10^{14}$	$2.2 \times 10^8$ $3 \times 10^{10}$	$3.9 \times 10^{10}$ $3 \times 10^{10}$	$2.8 \times 10^{11}$ $3 \times 10^{10}$	Diff: (calculated)	
2	$3.4 \times 10^{13} \exp (-225,000/RT)$ $3 \times 10^{14}$	$3.9 \times 10^8$ $3 \times 10^{10}$	$9.5 \times 10^8$ $3 \times 10^{10}$	$3.9 \times 10^7$ $3 \times 10^{10}$	Diff: (calculated)	
3	$6.7 \times 10^{12} \exp (-99,500/RT)$ $3 \times 10^{13} \exp (-6,000/RT)$	$2.9 \times 10^7$ $1.4 \times 10^{13}$	$3.2 \times 10^8$ $1.5 \times 10^{13}$	$1.7 \times 10^8$ $1.3 \times 10^{13}$	Diff: (calculated)	
4	$4.6 \times 10^{15} \exp (-24,600/RT)$ $6 \times 10^{15} \exp (900/RT)$	$2.1 \times 10^{14}$ $6.7 \times 10^{13}$	$3.9 \times 10^{14}$ $6.6 \times 10^{13}$	$6.0 \times 10^{14}$ $6.5 \times 10^{13}$	Diff: (calculated)	
5	$2.7 \times 10^{14} T^{-1} \exp (-125,400/RT)$ $1.5 \times 10^{15} T^{-1}$	$1.1 \times 10^4$ $3.9 \times 10^{11}$	$2.0 \times 10^4$ $3 \times 10^{11}$	$1.3 \times 10^6$ $2.5 \times 10^{11}$	Diff: (calculated)	
6	$6 \times 10^{14} T^{-1.5} \exp (-15,900/RT)$ $8.0 \times 10^{16} T^{-1.5}$	$3.3 \times 10^8$ $3.2 \times 10^{11}$	$3.5 \times 10^8$ $1.8 \times 10^{11}$	$3.4 \times 10^8$ $1.9 \times 10^{11}$	Diff: (calculated)	
7	$1.1 \times 10^{12} \exp (-50,600/RT)$ $5 \times 10^{11} \exp (-2,500/RT)$	$2 \times 10^8$ $3.9 \times 10^{11}$	$7 \times 10^8$ $6.3 \times 10^{11}$	$1.7 \times 10^{10}$ $6.5 \times 10^{11}$	Diff: (calculated)	
8	$3.7 \times 10^{14} T^{-1/2} \exp (-80,000/RT)$ $1.8 \times 10^{14} T^{-1/2}$	$2.7 \times 10^8$ $2.9 \times 10^{12}$	$1.7 \times 10^8$ $1.5 \times 10^{12}$	$6.2 \times 10^8$ $2.5 \times 10^{12}$	Diff: (calculated)	
9	$6 \times 10^{14} T^{-3/2} \exp (-14,800/RT)$ $3.4 \times 10^{14} T^{-3/2}$	$3.7 \times 10^8$ $2.2 \times 10^8$	$3.9 \times 10^8$ $1.5 \times 10^8$	$3.2 \times 10^8$ $1.1 \times 10^8$	Diff: (calculated)	
10	$6 \times 10^{14} T^{-3/2} \exp (-91,000/RT)$ $1.7 \times 10^{16} T^{-1.5}$	$2.9 \times 10^4$ $6.8 \times 10^{10}$	$1.7 \times 10^5$ $1.5 \times 10^{10}$	$6.6 \times 10^5$ $3.7 \times 10^{10}$	Diff: (calculated)	
11	$6 \times 10^{14} T^{-3/2} \exp (-134,000/RT)$ $1.1 \times 10^{12} T^{-1.5}$	$1.2 \times 10^8$ $4.4 \times 10^8$	$2.6 \times 10^8$ $3.1 \times 10^8$	$1.9 \times 10^8$ $2.1 \times 10^8$	Diff: (calculated)	
12	$2.4 \times 10^{15} \exp (-149,900/RT)$ $6 \times 10^{14}$	$1.8 \times 10^7$ $6 \times 10^{14}$	$7.6 \times 10^8$ $6 \times 10^{14}$	$9.0 \times 10^8$ $6 \times 10^{14}$	Diff: (calculated)	
13	$7.8 \times 10^{11} \exp (-45,400/RT)$ $2.1 \times 10^{12}$	$2.9 \times 10^8$ $2.1 \times 10^{12}$	$8.8 \times 10^8$ $2.1 \times 10^{12}$	$1.8 \times 10^8$ $2.1 \times 10^{12}$	Diff: (calculated)	
14	$1.9 \times 10^{11} T^{-1.5}$ $6 \times 10^{14} T^{-3/2} \exp (-3,600/RT)$	$7.6 \times 10^8$ $8.2 \times 10^8$	$3.5 \times 10^8$ $7.1 \times 10^8$	$4.1 \times 10^8$ $6.5 \times 10^8$	Diff: (calculated)	
15	$6.4 \times 10^{11} (\pi/1000)^{1/2} \exp (-34,100/RT)$ $3.2 \times 10^{12} (\pi/1000)^{1/2} \exp (-6,200/RT)$	$1.1 \times 10^{10}$ $2.9 \times 10^{12}$	$3.2 \times 10^{10}$ $3.9 \times 10^{12}$	$6.5 \times 10^{10}$ $4.7 \times 10^{11}$	Diff: (calculated)	
16	$1.8 \times 10^{16} T^{-1/2}$ $1.9 \times 10^{16} T^{-1/2} \exp (-72,600/RT)$	$2.9 \times 10^{14}$ $3.5 \times 10^{12}$	$2.5 \times 10^{14}$ $1.5 \times 10^{13}$	$2.3 \times 10^{14}$ $6.4 \times 10^{13}$	Diff: (calculated)	
17	$6.8 \times 10^{16} T^{-3/2}$ $6 \times 10^{16} T^{-3/2} \exp (-114,400/RT)$	$2.7 \times 10^{11}$ $1.6 \times 10^8$	$1.9 \times 10^{11}$ $1.9 \times 10^8$	$1.5 \times 10^{11}$ $9.7 \times 10^8$	Diff: (calculated)	





The list of reaction rate coefficients shown on pages 9 and 10 were obtained by simple collision theory as outlined,<sup>6</sup> if not otherwise stated. Where a name is given and the word "calculated," this particular constant has been calculated by means of the equilibrium constant and the other given rate constant. Numerical values are given for the three temperatures considered. For each reaction, two rate coefficients are listed. The first one applies to the forward, the second one applies to the reverse direction.

### ESTIMATED CONCENTRATION PROFILES FOR ALL SPECIES

For the three shock conditions considered, the following values for the concentrations will be calculated or taken from outside sources: (a) Initial concentration slopes immediately behind the shock front for all species ( $O_2$ ,  $N_2$ ,  $O$ ,  $N$ ,  $NO$ ,  $NO_2$ ,  $N_2O$ ,  $O_3$ , and  $NO_3$ ) will be calculated from reactions involving only  $N_2$  and  $O_2$ ; (b) the concentrations of the dominant species in the transition zone will be taken from Duff and Davidson<sup>1</sup> for the two points where  $N$  and  $NO$  show a maximum, while the concentrations of the added species will be calculated by using the steady-state approximation for these species; (c) the concentrations of all species in the equilibrium region will be taken from Duff and Davidson,<sup>1</sup> and Gilmore.<sup>5</sup>

a. The following reaction equations apply for the initial concentration slopes immediately behind the shock wave (point s at  $x = 0$ ):

Dominant Species:

$$-\frac{d(O_2)}{dt} = k_{1f} (O_2)(M) + k_{3f} (O_2)^2 + \left( k_{22r} + k_{30r} + k_{33r} \right) (N_2) (O_2)$$

$$-\frac{d(N_2)}{dt} = k_{2f} (N_2)(M) + \left( k_{22r} + k_{30r} + k_{33r} \right) (N_2) (O_2)$$

$$\frac{d(O)}{dt} = 2k_{1f} (O_2)(M)$$

$$\frac{d(N)}{dt} = 2k_{2f} (N_2)(M)$$

$$\frac{d(NO)}{dt} = 2k_{22r} (N_2) (O_2)$$

# Non-Dominant Species:

$$\frac{d(O_3)}{dt} = k_{3f} (O_2)^2$$

$$\frac{d(NO_2)}{dt} = k_{30r} (N_2)(O_2)$$

$$\frac{d(N_2O)}{dt} = k_{33r} (N_2)(O_2)$$

$$\frac{d(NO_3)}{dt} = 0$$

The initial values of  $O_2$ ,  $N_2$ , and  $M$  are taken from Duff and Davidson.<sup>1</sup> With minor deviations, they are (for all three shock conditions, i.e.  $T_s = 5000, 7000$ , and  $10,000^\circ K$ , respectively)

$$(O_2) = 1 \times 10^{-7} \text{ moles/cc}$$

$$(N_2) = 3 \times 10^{-7} \text{ moles/cc}$$

$$(M) = 4 \times 10^{-7} \text{ moles/cc}$$

so that the initial concentration slopes (in moles per cubic centimeter-second) are:

## Dominant Species:

$M$	$= 9.96$	$= 12.06$	$= 14.71$
$(O_2)$	$1.6 \times 10^{-3}$	$4.4 \times 10^{-2}$	$5.6 \times 10^{-1}$
$(N_2)$	$1.4 \times 10^{-5}$	$3.9 \times 10^{-4}$	$3.9 \times 10^{-3}$
$(O)$	$7.8 \times 10^{-4}$	$8.8 \times 10^{-2}$	$1.1 \times 10^0$
$(N)$	$2.3 \times 10^{-7}$	$7.2 \times 10^{-5}$	$8.5 \times 10^{-3}$
$(NO)$	$1.5 \times 10^{-5}$	$7.8 \times 10^{-4}$	$7.8 \times 10^{-3}$

# Non-Dominant Species

(NO <sub>2</sub> )	9.6 x 10 <sup>-9</sup>	2.2 x 10 <sup>-7</sup>	2.1 x 10 <sup>-6</sup>
(N <sub>2</sub> O)	1.1 x 10 <sup>-8</sup>	1.6 x 10 <sup>-7</sup>	1.2 x 10 <sup>-6</sup>
(O <sub>3</sub> )	3.2 x 10 <sup>-6</sup>	5.6 x 10 <sup>-5</sup>	4.8 x 10 <sup>-4</sup>
(NO <sub>3</sub> )	0	0	0

It can be seen from these values that the initial slopes of the dominant species (except for O<sub>2</sub> and H<sub>2</sub>, which have a negative slope) is larger by at least one order of magnitude than all the minor constituents.

b. To calculate the concentrations of the added species in the transition zone, the steady-state approximation will be used. This approach requires that the rate of change of the added species is negligibly small as well as the concentrations themselves. Therefore, it is sufficient to form or decompose the minor constituents by the dominant species only.

$$\begin{aligned} \frac{d(O_3)}{dt} &= k_{3f} (O_2)^2 - k_{3r} (O_3) (O) - k_{4f} (M) (O_3) + k_{4r} (O_2) (O) (M) \\ &\quad + k_{5f} (NO) (O_2) - k_{5r} (N) (O_3) \\ (O_3) &\approx \frac{k_{3f} (O_2)^2 + k_{4r} (O_2) (O) (M) + k_{5f} (NO) (O_2)}{k_{3r} (O) + k_{4f} (M) + k_{5r} (N)} \end{aligned}$$

$$\frac{d(\text{NO}_2)}{dt} = k_{16f} (\text{NO})(\text{O})(\text{M}) - k_{16r} (\text{NO}_2)(\text{M}) + k_{13f} (\text{NO})(\text{O}_2) - k_{13r} (\text{O})(\text{NO}_2)$$

$$+ k_{20} (\text{NO})^2 - k_{20r} (\text{N})(\text{NO}) + k_{26r} (\text{M})(\text{N})(\text{O}_2) - k_{26f} (\text{NO}_2)(\text{M})$$

$$- k_{30} (\text{NO}_2)(\text{N}) + k_{30r} (\text{N}_2)(\text{O}_2)$$

$$(\text{NO}_2) \approx \frac{k_{16f} (\text{NO})(\text{O})(\text{M}) + k_{13f} (\text{NO})(\text{O}_2) + k_{20f} (\text{NO})^2 + k_{26r} (\text{M})(\text{N})(\text{O}_2) + k_{30r} (\text{N}_2)(\text{O}_2)}{k_{16r} (\text{M}) + k_{13r} (\text{O}) + k_{20r} (\text{N}) + k_{26f} (\text{M}) + k_{30f} (\text{N})}$$

$$\frac{d(\text{N}_2\text{O})}{dt} = k_{17f} (\text{NO})(\text{N})(\text{M}) - k_{17r} (\text{N}_2\text{O})(\text{M}) + k_{21f} (\text{NO})^2 - k_{21r} (\text{O})(\text{N}_2\text{O})$$

$$+ k_{19f} (\text{NO})(\text{N}_2) - k_{19r} (\text{N}_2\text{O})(\text{N}) - k_{31f} (\text{N}_2\text{O})(\text{M}) + k_{31r} (\text{M})(\text{N}_2)(\text{O})$$

$$- k_{33f} (\text{N}_2\text{O})(\text{O}) + k_{33r} (\text{N}_2)(\text{O}_2)$$

$$(\text{N}_2\text{O}) \approx \frac{k_{17f} (\text{NO})(\text{N})(\text{M}) + k_{21f} (\text{NO})^2 + k_{19f} (\text{NO})(\text{N}_2) + k_{31r} (\text{M})(\text{N}_2)(\text{O}) + k_{33r} (\text{N}_2)(\text{O}_2)}{k_{17r} (\text{M}) + k_{21r} (\text{O}) + k_{19r} (\text{N}) + k_{31f} (\text{M}) + k_{33f} (\text{O})}$$

$$\frac{d(\text{NO}_3)}{dt} = k_{14f} (\text{NO})(\text{O}_2)(\text{M}) - k_{14r} (\text{NO}_3)(\text{M})$$

$$(\text{NO}_3) \approx \frac{k_{14f} (\text{NO})(\text{O}_2)(\text{M})}{k_{14r} (\text{M})}$$

The tabulation on the following page lists the concentrations (in moles per cubic centimeters) of the dominant species as taken from Duff and Davidson<sup>1</sup> and of the added species as calculated by the above equations at the two locations where the concentrations of NO and N are maximum.

Specie	<u>4,000°K</u>		<u>5,000°K</u>		<u>6,000°K</u>	
	$\frac{\theta_t^I}{\theta_t^{II}}$	$\frac{\theta_t^{II}}{\theta_t^I}$	$\frac{\theta_t^I}{\theta_t^{II}}$	$\frac{\theta_t^{II}}{\theta_t^I}$	$\frac{\theta_t^I}{\theta_t^{II}}$	$\frac{\theta_t^{II}}{\theta_t^I}$
N <sub>2</sub>	3.4 x 10 <sup>-7</sup>	3.8 x 10 <sup>-7</sup>	3.7 x 10 <sup>-7</sup>	4 x 10 <sup>-7</sup>	3.9 x 10 <sup>-7</sup>	4.8 x 10 <sup>-7</sup>
O <sub>2</sub>	7 x 10 <sup>-8</sup>	4.4 x 10 <sup>-8</sup>	4.2 x 10 <sup>-8</sup>	1.3 x 10 <sup>-8</sup>	4.1 x 10 <sup>-8</sup>	~ 5 x 10 <sup>-10</sup>
N	4 x 10 <sup>-10</sup>	1.6 x 10 <sup>-10</sup>	5.4 x 10 <sup>-9</sup>	3.4 x 10 <sup>-9</sup>	3.7 x 10 <sup>-8</sup>	7.8 x 10 <sup>-8</sup>
O	3.3 x 10 <sup>-8</sup>	1 x 10 <sup>-7</sup>	1.1 x 10 <sup>-7</sup>	1.7 x 10 <sup>-7</sup>	1.8 x 10 <sup>-7</sup>	2.5 x 10 <sup>-7</sup>
NO	4.4 x 10 <sup>-9</sup>	3 x 10 <sup>-8</sup>	1.7 x 10 <sup>-8</sup>	3.4 x 10 <sup>-8</sup>	3.4 x 10 <sup>-8</sup>	1.1 x 10 <sup>-8</sup>
M	4.5 x 10 <sup>-7</sup>	5.5 x 10 <sup>-7</sup>	5.4 x 10 <sup>-7</sup>	6.2 x 10 <sup>-7</sup>	6.4 x 10 <sup>-7</sup>	8.2 x 10 <sup>-7</sup>
O <sub>3</sub>	2.2 x 10 <sup>-15</sup>	5.7 x 10 <sup>-15</sup>	3.5 x 10 <sup>-15</sup>	6.1 x 10 <sup>-15</sup>	1.6 x 10 <sup>-15</sup>	1.5 x 10 <sup>-15</sup>
NO <sub>2</sub>	5.2 x 10 <sup>-13</sup>	2.0 x 10 <sup>-12</sup>	8.9 x 10 <sup>-13</sup>	5.5 x 10 <sup>-13</sup>	2.9 x 10 <sup>-14</sup>	1 x 10 <sup>-14</sup>
N <sub>2</sub> O	1.2 x 10 <sup>-14</sup>	3.8 x 10 <sup>-14</sup>	4 x 10 <sup>-14</sup>	7.0 x 10 <sup>-14</sup>	7.2 x 10 <sup>-14</sup>	1.2 x 10 <sup>-13</sup>
NO <sub>3</sub>	3.0 x 10 <sup>-19</sup>	1.0 x 10 <sup>-18</sup>	5.3 x 10 <sup>-19</sup>	3.2 x 10 <sup>-19</sup>	9.2 x 10 <sup>-20</sup>	2.5 x 10 <sup>-20</sup>

It is seen that the approximated concentrations of the added species are smaller by several orders of magnitude than the concentrations of the postulated dominant species.

c. As the final step in estimating the concentration profiles, the equilibrium values of the concentrations are considered. They are taken from tables compiled by Gilmore<sup>5</sup> in which the cold gas state of mixture is not assumed to be a pure nitrogen-oxygen mixture but rather an idealized air mixture with 78% N<sub>2</sub>, 21% O<sub>2</sub>, 0.9% Ar, 0.03% CO<sub>2</sub>, and 0.03% Ne. However, the inclusion of 1% "impurities" will not affect appreciably the high-temperature composition of an original pure N<sub>2</sub>-O<sub>2</sub> mixture. The temperature has been chosen as indicated in the tabulation (see page 4) and the density ratio as 10<sup>-2</sup>. The concentrations are given in particles per cold air particles. To convert to mole per mole air, the concentrations have to be multiplied by 1.991. Further on, to convert to mole per cubic centimeter the values have to be multiplied by  $\rho/\mu$  where  $\rho$  is the equilibrium mixture and  $\mu$  the mole weight. This later factor is taken approximately as 29 gm/mole.

M	9.96	12.06	14.71
(N <sub>2</sub> )	$7.6 \times 10^{-7}$	$7.6 \times 10^{-7}$	$6.6 \times 10^{-7}$
(O)	$2.3 \times 10^{-7}$	$3.9 \times 10^{-7}$	$4.1 \times 10^{-7}$
(H)	$1.6 \times 10^{-9}$	$4.0 \times 10^{-8}$	$2.2 \times 10^{-7}$
(NO)	$3.4 \times 10^{-8}$	$1.7 \times 10^{-8}$	$8.2 \times 10^{-9}$
(O <sub>2</sub> )	$8.2 \times 10^{-8}$	$4.2 \times 10^{-9}$	$3.8 \times 10^{-10}$
(O <sub>3</sub> )	$1.1 \times 10^{-14}$	$5.6 \times 10^{-16}$	$3.4 \times 10^{-17}$
(NO <sub>2</sub> )	$3.8 \times 10^{-12}$	$3.2 \times 10^{-13}$	$3.4 \times 10^{-14}$
(N <sub>2</sub> O)	$< 10^{-12}$	$< 10^{-13}$	$< 10^{-14}$
(NO <sub>3</sub> )	$< 10^{-12}$	$< 10^{-13}$	$< 10^{-14}$

The equilibrium concentrations of (N<sub>2</sub>O) and (NO<sub>3</sub>) are not listed by Gilmore.<sup>5</sup> But, since they are less stable than (NO<sub>2</sub>) at this temperature, it is safe to assume that the concentrations of these two species are smaller than the one of (NO<sub>2</sub>).

### RELATIVE SIGNIFICANCE OF REACTIONS

The reaction rates involving the major and minor constituents will now be estimated. This is done by substituting the values for the concentrations and the rate coefficients into the reaction equations for  $T = 4000, 5000, \text{ and } 6000^\circ\text{K}$ , respectively.

First, the contributions of the additional species to the rates of formation and decomposition of the major constituents will be calculated for the point in the concentration profile at which NO has a maximum. The absolute values for the net change are as follows

	<u>Major Species</u>		
	<u>4000°K</u>	<u>5000°K</u>	<u>6000°K</u>
$\text{O}_2$	$3.1 \times 10^{-5}$	$3.1 \times 10^{-3}$	$1.0 \times 10^{-3}$
$\text{N}_2$	$1.0 \times 10^{-4}$	$4.0 \times 10^{-4}$	$1.0 \times 10^{-2}$
O	$3.0 \times 10^{-5}$	$3.1 \times 10^{-3}$	$1.1 \times 10^{-3}$
N	$1.1 \times 10^{-4}$	$4.5 \times 10^{-4}$	$1.0 \times 10^{-2}$
NO	$8.6 \times 10^{-5}$	$3.6 \times 10^{-4}$	$9.9 \times 10^{-3}$

	<u>Minor Species</u>		
	<u>4000°K</u>	<u>5000°K</u>	<u>6000°K</u>
$\text{O}_2$	$2.9 \times 10^{-6}$	$3.0 \times 10^{-6}$	$1.1 \times 10^{-6}$
$\text{N}_2$	$4.0 \times 10^{-7}$	$1.0 \times 10^{-6}$	$1.2 \times 10^{-5}$
O	$4.6 \times 10^{-6}$	$7.7 \times 10^{-6}$	$1.3 \times 10^{-5}$
N	$3.7 \times 10^{-9}$	$2.8 \times 10^{-6}$	$1.5 \times 10^{-7}$
NO	$3.6 \times 10^{-6}$	$2.2 \times 10^{-6}$	$2.1 \times 10^{-6}$

It is seen that the contributions of the minor species are smaller by at least one order of magnitude.

Next, the individual contributions to the rate of formation and decomposition will be illustrated in Figure 1. The rates of formation and decomposition of the five major species ( $O_2$ ,  $N_2$ ,  $O$ ,  $N$ , and  $NO$ ) are represented by points for the three shock conditions considered. The concentration of the dominant species are taken from Duff and Davidson,<sup>1</sup> whereas the concentrations of the added species are taken from the approximate calculations of the previous section in this report. All concentrations have been taken at the point where  $NO$  has a maximum. The points representing the reaction rates are then connected by lines for better illustration. The reaction rates as obtained from the restricted reaction scheme as given<sup>1</sup> [namely Equation (1), (2), (12), (15), and (18)] are shown in detail. The reaction rates resulting from the additional reaction equations have been summed and are indicated by the symbol  $\Sigma$ . The rates of formation are given in solid lines and the rates of the decomposition in dotted lines. Figure 2 presents in detail the reaction rates involving the minor constituents which had been used to calculate the sum ( $\Sigma$ ) of the previous plot.

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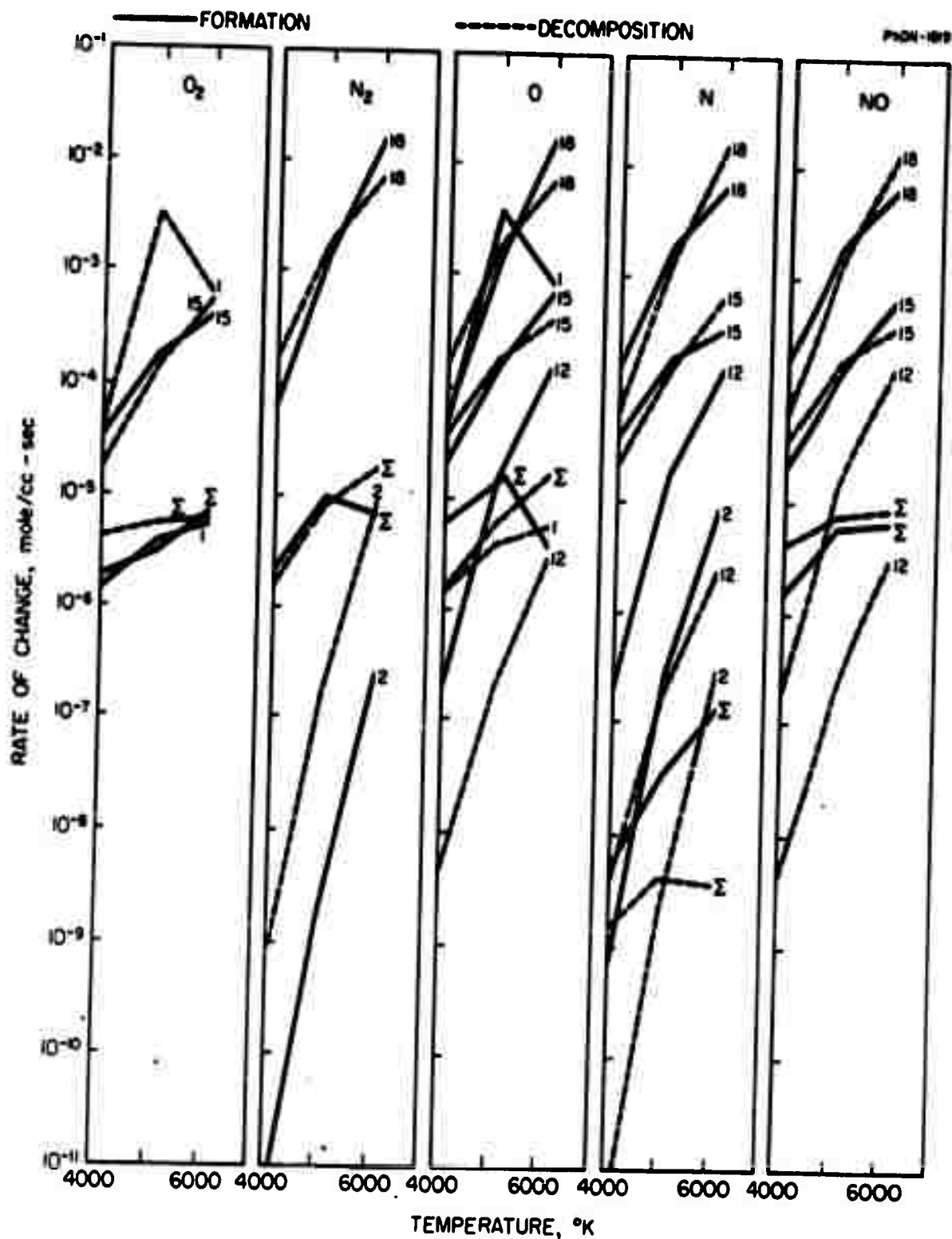


FIGURE 1 RATES OF FORMATION AND DECOMPOSITION OF THE DOMINANT SPECIES BY  
 (a) REACTION PATHS (1, 2, 12, 15 AND 18)  
 CONNECTING THESE (DOMINANT) SPECIES ONLY  
 (b) SUM OF REACTION PATHS INVOLVING NON-DOMINANT SPECIES ( $\Sigma$ )  
 AS A FUNCTION OF TEMPERATURE

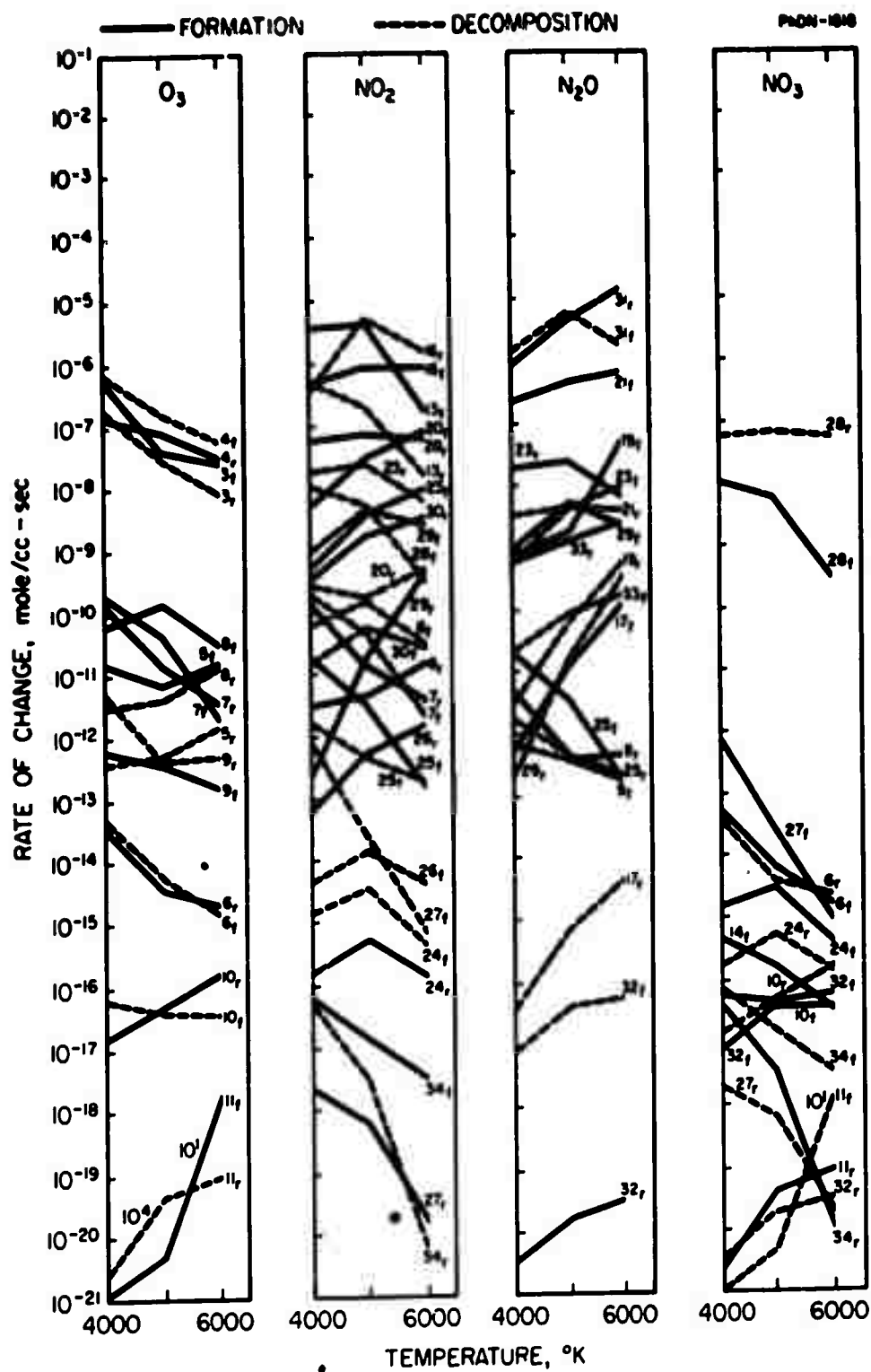


FIGURE 2 RATES OF FORMATION AND DECOMPOSITION OF THE NON-DOMINANT SPECIES INVOLVING ALL SPECIES AS A FUNCTION OF TEMPERATURE

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